NEXT-GENERATION NITRIC ACID PRODUCTION: TOTAL RECYCLE AND ALTERNATIVE CONCEPTS

STAMICARBON
NEXTCHEM Sustainable Technology Solutions

NEXTCHEM

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SUMMARY

1 ABSTRACT

The production of nitric acid is a critical process in the chemical industry, particularly for the fertilizer sector. This paper explores innovative approaches to nitric acid production, with a primary focus on the NX Stami™ Nitrates Total Recycle concept, which simultaneously reduces capital expenditure (CAPEX), operating expenditure (OPEX), and environmental impact. This new process concept integrates pure oxygen into the nitric acid flowsheet, eliminating the need for atmospheric air injection and allowing continuous recycling of nitrogen within the system. As a result, large air-handling systems are no longer required, which significantly reduces equipment size, process complexity, and energy consumption. Detailed process evaluation shows that the use of pure O_2 enhances oxidation efficiency, improves NO_x conversion, and lowers N_2O and NO_x emissions compared with conventional air-based routes.

The paper also describes additional routes to improve plant efficiency using pure oxygen. These options represent suitable alternatives for plant revamps, allowing for capacity increases and reductions in operating costs and emissions with relatively low capital investment.

Overall, this study provides an analysis of these concepts, highlighting their potential to modernize nitric acid production and contribute to a more sustainable industrial landscape.

2 INTRODUCTION

As global awareness of environmental issues grows, the industrial sector faces increasing pressure to adopt greener practices. The necessity of becoming greener in industry is driven by several factors. Firstly, industrial activities significantly contribute to pollution, resource depletion, and greenhouse gas emissions. Transitioning to greener practices helps mitigate these negative impacts, preserving natural resources and protecting ecosystems. Additionally, governments worldwide are implementing stricter environmental regulations. Industries must comply with these regulations to avoid penalties and maintain their operating licenses.

Moreover, modern consumers are more environmentally conscious and prefer products from companies that prioritize sustainability. Adopting green practices can enhance a company's reputation and attract eco-conscious customers. Green manufacturing processes often lead to increased efficiency and reduced waste, resulting in cost savings. Sustainable practices ensure the long-term viability of industries by reducing dependency on finite resources and minimizing environmental risks.

Technology licensors play a crucial role in helping industries transition to greener practices by providing access to advanced technologies and expertise. They offer innovative technologies that can enhance production efficiency and reduce environmental impact.

Stamicarbon, the nitrogen technology licensor of NEXTCHEM (MAIRE Group), is committed to continuous improvement of its licensed processes, with a strong focus on adapting to the green transition and engaging in sustainable practices. The company is at the forefront of developing and implementing innovative technologies that reduce environmental impact and promote sustainability.

Stamicarbon recognizes the critical role it plays in this transition and has made significant strides in enhancing its technology portfolio to support sustainable development. The company's commitment to sustainability is evident in its efforts to reduce carbon emissions, improve energy efficiency, and minimize waste in the production processes it licenses.

One of the key areas where Stamicarbon has made substantial progress is in the development of its NX Stami™ Ammonia and NX Stami™ Nitrates division: ammonia, nitric acid and ammonium nitrate technology. Furthermore, integrating these technologies presents a significant opportunity to design and implement more sustainable downstream processes such as nitric acid production. This integration not only enhances the overall efficiency of the production chain but also paves the way for innovative approaches that reduce environmental impact, ultimately supporting the global transition toward a more eco-friendly and resilient industrial landscape.

3 CONVENTIONAL NITRIC ACID PRODUCTION

Nitric acid is a crucial chemical compound. Approximately 80% of its global production is dedicated to the fertilizer industry, where it is essential in the manufacture of both solid and liquid fertilizers.

In the production of solid fertilizers, nitric acid is used to produce compounds such as Calcium Ammonium Nitrate and Fertilizer Grade Ammonium Nitrate. These fertilizers are crucial for enhancing soil fertility and promoting healthy crop growth. Additionally, nitric acid is a key component in the production of liquid fertilizers, such as Urea Ammonium Nitrate. In this process, ammonium nitrate solution is mixed with urea solution, resulting in a highly effective liquid fertilizer that provides essential nutrients to plants. The widespread use of nitric acid in these applications underscores its importance in supporting global agricultural productivity and sustainability.

Stamicarbon provides both mono-pressure (see Figure 1) and dual-pressure (see Figure 2) nitric acid production processes, catering to a wide range of plant capacities. The mono-pressure design is ideal for lower plant capacities, up to 600 metric ton per day (MTPD), while the dual-pressure design is suitable for capacities higher than 600 MTPD.

The production of nitric acid is primarily carried out using the Ostwald process, which involves several key steps. First, ammonia is oxidized on a platinum-rhodium (Pt/Rh) catalyst in the presence of excess oxygen at medium pressures (5 bara in dual-pressure and 8 bara in mono-pressure Stamicarbon technologies) and high temperatures (around 900 °C) to produce nitrogen monoxide (NO) and water. This reaction is highly exothermic (-226 KJ/mol of NO formed), releasing a significant amount of heat.

Next, NO is further oxidized to nitrogen dioxide (NO_2) in the presence of excess oxygen. This step occurs at lower temperatures (< 490 °C) and is a slower, non-catalytic reaction.

Finally, NO_2 is absorbed in water, resulting in the formation of nitric acid (HNO_3) and additional NO, which is further oxidized to NO_2. While mono-pressure technology works at constant pressure of 8 bara, in dual-pressure technology, the absorption section operates at 11 bara.

The overall chemical reactions can be summarized as follows:

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad \text{(reaction 1)}$$

$$2NO + O_2 \rightarrow 2NO_2 \qquad \text{(reaction 2)}$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO \qquad \text{(reaction 3)}$$

In the Pt/Rh gauzes, the following undesired side reactions also take place:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad \text{(reaction 4)}$$

$$4NH_3 + 4O_2 \rightarrow 2N_2O + 6H_2O \qquad \text{(reaction 5)}$$

The nitric acid produced is typically a diluted solution (usually 60% by weight), which can be further concentrated if needed.

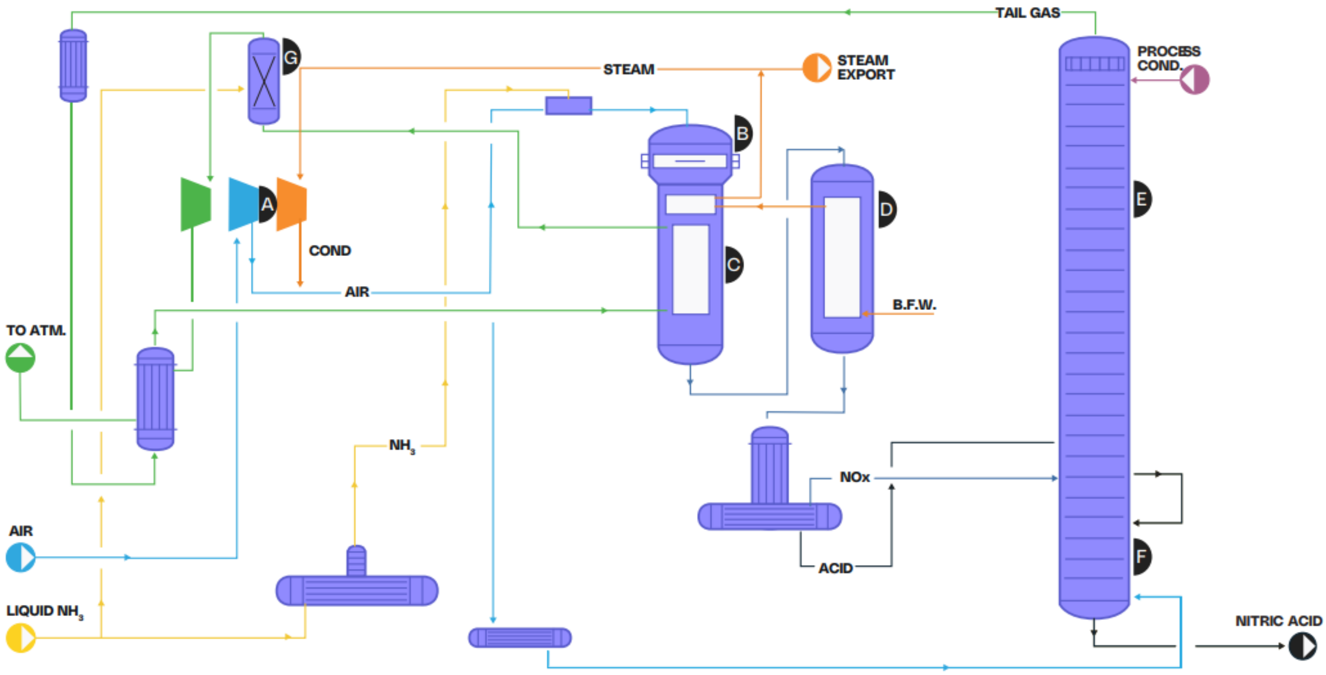

Figure 1: Process scheme of Stamicarbon's mono-pressure nitric acid technology.

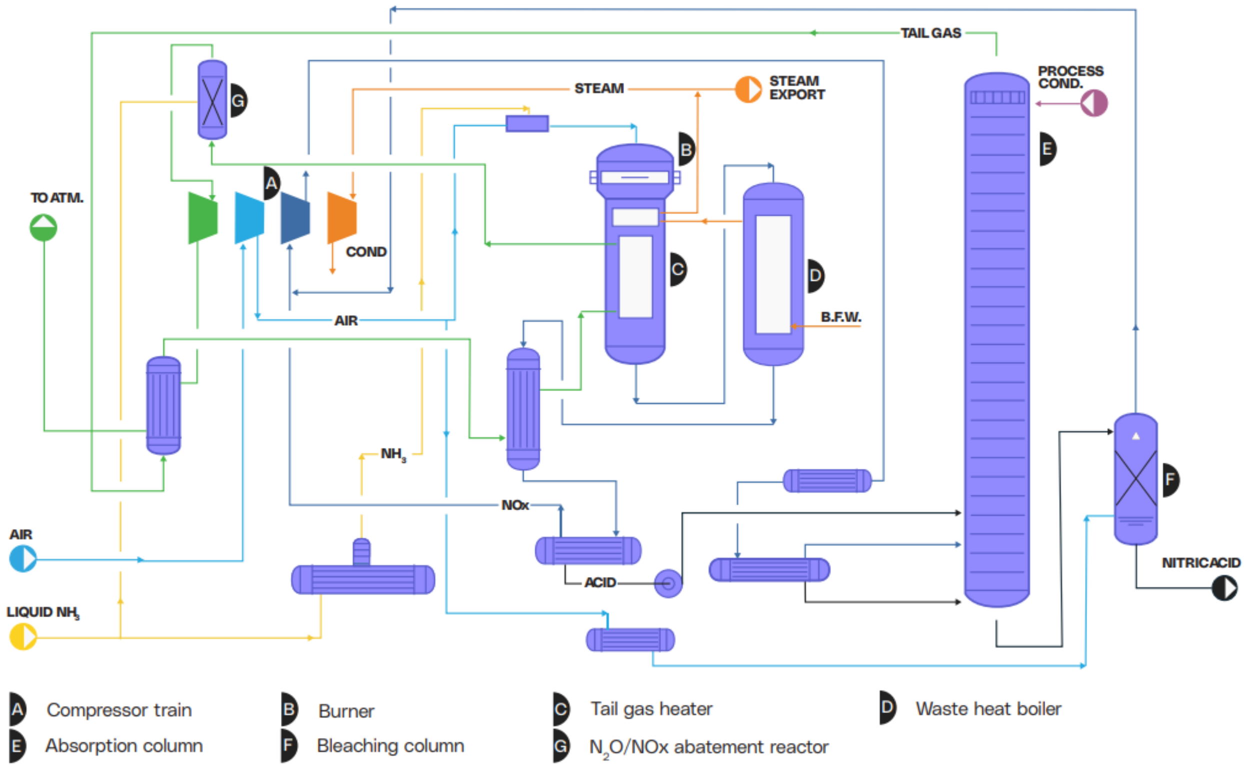

Figure 2: Process scheme of Stamicarbon's dual-pressure nitric acid technology.

In standard nitric acid production, atmospheric air is utilized as the carrier for the oxygen required in the oxidation reactions (reactions 1 and 2) of the nitric acid production process. Given that atmospheric air contains approximately 21% by mol oxygen and 79% by mol nitrogen, a substantial amount of nitrogen is continuously compressed and subsequently released into the atmosphere (so-called tail gas) in the standard one-through process. The amount of tail gas released to the atmosphere is approximately 3250 Nm^3/ton HNO_3 (100%).

Still, nitrogen plays a crucial role in nitric acid production, and the process cannot operate safely without nitrogen being present. It acts as a buffer, helping to retain the heat generated during the ammonia oxidation reaction and ensuring proper functioning of the equipment. By absorbing and redistributing heat, nitrogen ensures that the highly exothermic ammonia oxidation reaction proceeds smoothly and safely.

Moreover, nitrogen helps to maintain the NH_3 concentration at the inlet of the NH_3 burner below the Lower Explosive Limit of the NH_3/air mixture, thereby preventing the formation of an explosive mixture. At the ammonia burner inlet, the NH_3/air ratio must remain below approx. 13% by volume to ensure the process stays within safe operational limits.

However, the continuous compression and decompression of such a large flow of inert material necessitates the use of complex rotating equipment. This equipment must be robust and reliable to handle high volumes of nitrogen and maintain the desired pressure levels throughout the process. The design and maintenance of this equipment are critical in ensuring the efficiency and longevity of the nitric acid production plant.

4 TOTAL RECYCLE CONCEPT FOR NITRIC ACID PRODUCTION

Stamicarbon has recently developed a pioneering nitric acid production process. This innovative process is distinguished by its use of only O_2 and NH_3 as the required consumed raw materials, with N_2 being continuously recirculated within the plant. By eliminating the need for a continuous flow of atmospheric air, the process avoids the constant compression and decompression of nitrogen gas. This results in a significant reduction in plant complexity, as the air compressor and expander typically used in standard nitric acid production can be omitted.

Moreover, the circulation of nitrogen (N_2) dramatically reduces the need to release a continuous stream into the atmosphere, thereby eliminating almost to zero the emissions of hazardous compounds such as nitrous oxide (N_2O) and nitrogen oxides (NO_x).

4.1 Process description

Stamicarbon's nitric acid total recycle concept (see Figure 3) uses ammonia and oxygen as raw materials and operates at 8 bara. Nitrogen is added to the system during plant startup and is recycled through the process until the next complete plant shutdown. During short shortages, nitrogen can remain inside the process without the need to fill the system again when starting up.

One of the most revolutionary features of this process is the addition of oxygen through the bleaching column at the back end of the plant. Its primary function is to act as a stripping medium to remove the last traces of dissolved NO_x from the nitric acid solution.

From the bleaching column, the O_2 is mixed with the process gas and sent to the oxidation/absorption column. In this column, nitrogen oxides are oxidized to form nitrogen dioxide, which is subsequently condensed to form nitric acid (see reactions 2 and 3 in Section 3). Process water is added at the top of the column. At the bottom, 60 wt% acid is produced and sent to the top of the bleaching column to remove the dissolved NO_x molecules.

At the top of the oxidation/absorption column, a mixture of nitrogen, oxygen, and traces of NO_x is boosted in the recycle compressor to overcome pressure drop across the process. This mixture has similar composition of oxygen and nitrogen as atmospheric air. After heating the synthetic air mixture to the right temperature, it is then mixed with NH_3 from battery limits in the correct ratio and sent to the NH_3 burner.

Here, as in the standard process, reactions 1, 4 and 5 (indicated in Section 3) occur on Pt/Rh gauzes, increasing the temperature of the mixture up to 900 °C. The N_2O formed on the gauzes is destroyed in a catalyst basket located underneath the gauzes (the so-called secondary catalyst), according to the following reaction:

$$2N_2O \rightarrow 2N_2 + O_2 \qquad \text{(reaction 6)}$$

From this point onward, the process mixture is cooled down. In this new concept, there is no need to heat the tail gas to high temperatures because it is replaced by recycle gas that is not discharged to the atmosphere and therefore requires a lower temperature. As a result, all the valuable reaction heat can be utilized to produce high-pressure steam.

Further along in the process, when the process gas temperature is lower, cooling water is used to reduce the temperature of the gas below its dew point, and a weak solution of nitric acid is formed. For that, a cooler condenser is used. The acid solution is sent to the right tray in the oxidation/absorption column, while the cooled gas is mixed with the gas outlet from the bleaching column (with high oxygen content) to enter at the bottom of the oxidation/absorption column.

In the process, nitrogen is produced in the gauzes (see reaction 4 in Section 3) as byproduct. For that reason, to avoid accumulation of this component and avoid pressure increase in the system, a continuous small purge (<0.02 ton/ton HNO_3 (100%)) is sent to the atmosphere. This purge is very small and, therefore, the concept does not foresee the need for an NO_x abatement reactor.

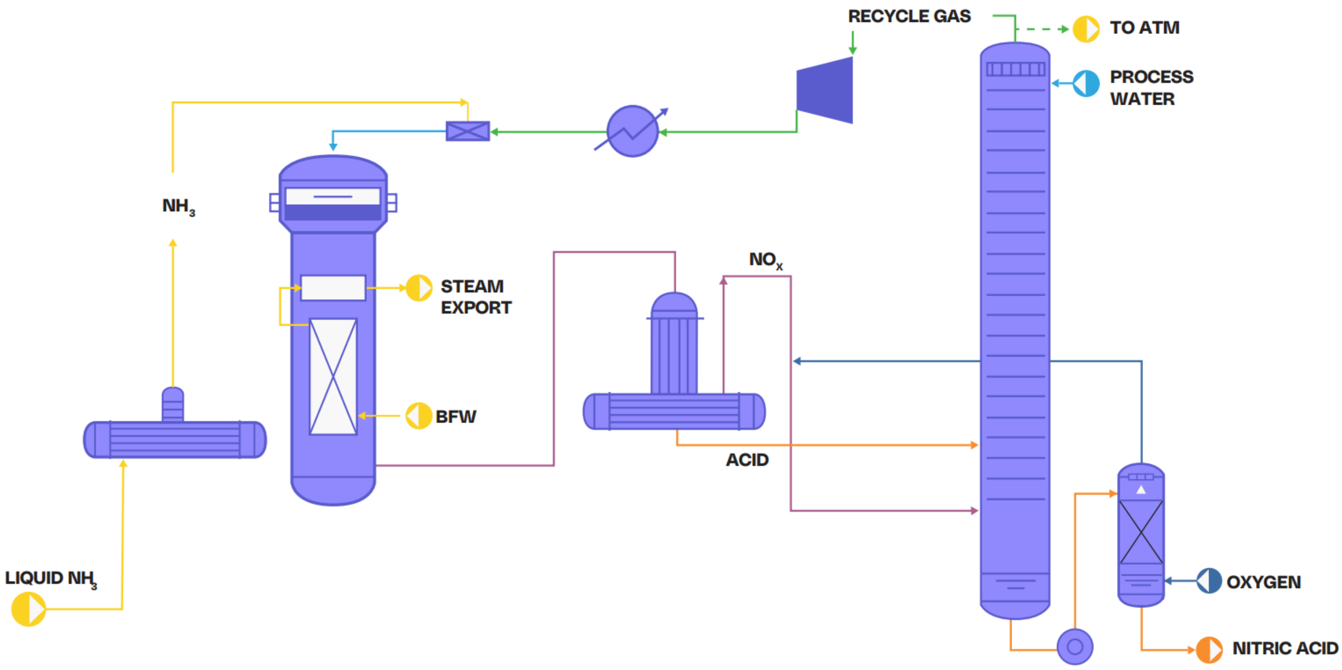

Figure 3: Stamicarbon's NX Stami™ Nitrates Total Recycle process scheme.

4.2 Main process advantages

The main advantage of the Total Recycle concept is its simplicity. The following pieces of equipment will be fully eliminated or decreased in size:

- Compressor train: There is no requirement for a complex compressor train as in the conventional process, since there is no continuous compression of air and decompression of tail gas.
- Oxidation/absorption column: The rich oxygen content of the gas entering the oxidation/absorption column promotes the oxidation of NO to NO_2, reducing the size of the column by almost half compared to existing processes on the market.
- Abatement reactor: Since the continuous tail gas stream is avoided, there is no continuous flow to the atmosphere, except for a small purge to avoid nitrogen accumulation in the system. Therefore, the tertiary abatement reactor is not required.
- Steam export: There is no need to heat the tail gas to temperatures of up to 480 °C, so most of the heat generated in the process is used to produce steam, resulting in high steam export rates.

In addition to these benefits, the Total Recycle concept can be applied across a wide range of capacities. The standard process pressure is 8 bara, which offers a good compromise between the oxidation and absorption sections. Oxidation of NH_3 to NO in Pt/Rh gauzes is more efficient at lower pressures, reducing precious metal losses, while absorption is enhanced at higher pressures. However, the process is flexible and can be designed for lower pressures (<8 bara) to further minimize precious metal losses. In this concept, the size of the oxidation/absorption column is significantly reduced compared to conventional processes, so operating the column at lower pressures does not result in large equipment.

All these advantages significantly impact the CAPEX and OPEX of the plant. By reducing the size and complexity of key equipment such as the compressor train, oxidation/absorption column, and abatement reactor, the initial capital investment required for the plant is substantially lowered. Additionally, the simplified process design leads to reduced maintenance costs and lower energy consumption, further decreasing operational expenses.

The elimination of continuous tail gas compression and decompression not only simplifies the process but also reduces the chance for equipment degradation, extending its lifespan and reliability. The enhanced steam export capability can be utilized for other plant operations or sold, providing an additional revenue stream.

Further in the paper, a detailed analysis of these cost savings is performed, highlighting the economic benefits of adopting the Total Recycle concept.

4.3 Oxygen supply cases

Nitric acid Total Recycle concept shows great synergy with ammonia production. The most common method of producing syngas is through primary steam methane reforming. This process involves natural gas (primarily methane) reacting with steam at high temperatures to produce hydrogen and carbon monoxide. Downstream the primary reforming unit, the secondary reformer plays a crucial role in adjusting the hydrogen-to-nitrogen ratio required for the ammonia synthesis reaction. In this stage, air is introduced into the reactor, improving the conversion of methane and providing the necessary nitrogen for the synthesis reaction.

Other methods to produce hydrogen (H_2) using hydrocarbons as raw material are autothermal reforming (ATR) and catalytic partial oxidation (CPO). In these cases, air separation units (ASUs) are required to supply the correct amount of nitrogen (N_2) to hydrogen (H_2) and, in case of CPO and ATR also oxygen (O_2) for the process.

When the CO_2 produced in these abovementioned processes is captured, the ammonia produced is known as blue ammonia.

As the industry moves towards more sustainable ammonia (NH_3) production routes, the discussion expands to include both pink and green ammonia. In both cases, hydrogen is supplied by electrolyzers, which split water into hydrogen and oxygen using electricity. Nitrogen is obtained via ASUs that use atmospheric air and separate the nitrogen molecules from it. The production of pink and green ammonia avoids the formation of CO_2, resulting in zero direct carbon emissions.

The primary difference between pink and green ammonia lies in the energy source used to power the electrolyzers and ASU. Green ammonia is produced using renewable energy sources such as solar, wind, or hydropower, ensuring that the entire process is carbon-free and sustainable. Pink ammonia is produced using nuclear power. Nuclear energy, while also low in carbon emissions, provides a consistent and reliable power supply, making it a viable option for ammonia production.

In green/pink ammonia production, oxygen is obtained as byproduct. Most of the oxygen is generated in the electrolyzers, with a smaller portion produced by the ASU. Electrolyzers can operate across a range of pressures, typically from atmospheric pressure up to 30 bar. Consequently, it is likely that the oxygen produced, often at pressures above 8 bara, can be supplied directly to the nitric acid plant without the need for additional compression. This represents the most favorable scenario, as it eliminates the need for an oxygen compressor and the associated energy consumption.

However, if the electrolyzers operate at a pressure lower than that required by the nitric acid process, an oxygen compressor will be necessary to meet process requirements.

Furthermore, the concept remains applicable even in scenarios where no oxygen is available and, instead, an air separation unit is installed and dedicated to supplying oxygen to the nitric acid plant. While this approach is less attractive from both CAPEX and OPEX perspectives, it remains a viable and logical option.

Additionally, blue and grey ammonia production processes that utilize ATR or CPO require an ASU. In such cases, designing a larger unit to accommodate additional oxygen demand presents a strategic opportunity.

To produce one ton of HNO_3, the total oxygen requirement in the nitric acid plant amounts to 1.04 ton of O_2.

4.3.1 Case Study: O_2 balance in green ammonia to nitrates route

Since the nitric acid Total Recycle concept is very attractive in combination with green ammonia, it is relevant to investigate the oxygen balance further. For that, in this section, the balances for ammonia to ammonium nitrate solution (ANS) are analyzed.

For nitric acid (HNO_3) production, approximately 0.285 ton of NH_3 are required per ton of HNO_3 (100%) produced. Similarly, for ANS production, around 0.215 ton of NH_3 are needed per ton of ANS.

Given that the nitric acid demand for ANS production is approximately 0.795 ton of HNO_3 per ton of ANS, it follows that roughly 0.440 ton of NH_3 are required to produce one ton of ANS (see Figure 4).

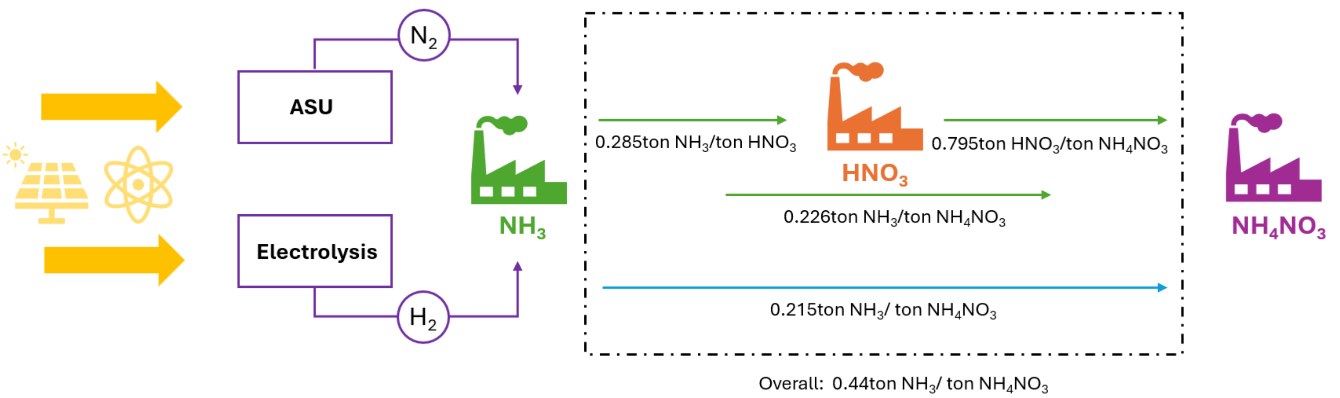

Figure 4: Ammonia demand in ANS production.

Since the primary focus is on oxygen availability for nitric acid production, it is more intuitive to express the overall ammonia demand in terms of nitric acid output. Given that 0.44 ton of NH_3 are required per ton of NH_4NO_3, approximately 0.55 ton of NH_3 are required per ton of HNO_3.

Now that the ammonia demand is calculated, oxygen availability can be derived from it. For every ton of NH_3 required, 1.6 ton of O_2 are produced through a combination of electrolyzers and an ASU. Of this 1.6 ton of O_2, approximately 1.4 ton come from the electrolyzers, while 0.2 ton are produced by the ASU. Although the contribution from the ASU is limited, the oxygen it produces is still valuable.

Considering the information mentioned above that 0.55 ton of NH_3 are required per ton of HNO_3 produced, the available amount of oxygen is 0.88 ton O_2/ton HNO_3 (100%) (as shown in Figure 5).

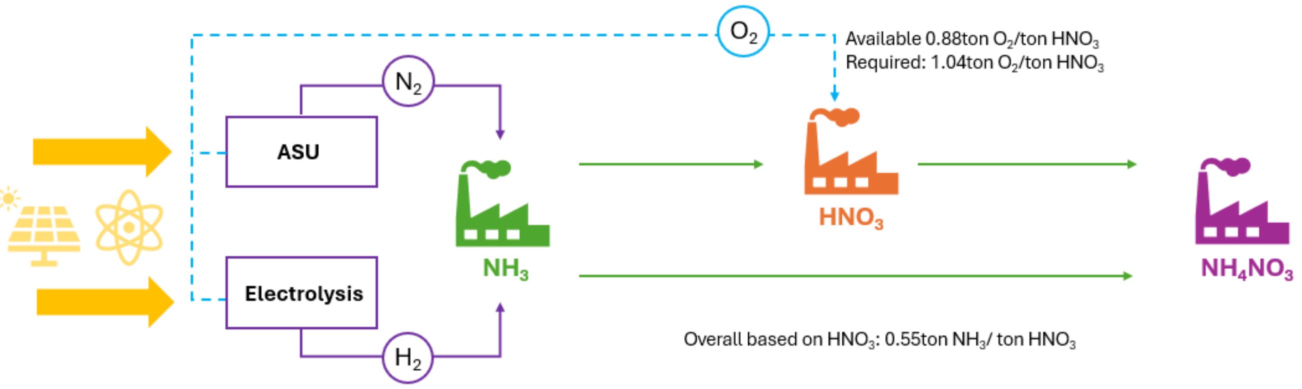

Figure 5: Oxygen availability and demand in ammonia to nitrates chain.

As demonstrated in the previous analysis, when ammonia production is exclusively allocated to nitrate production, a slight oxygen deficit arises within the nitric acid plant, requiring a small additional oxygen supply to sustain optimal operation.

If a higher volume of pure oxygen is needed, this shortfall can be compensated through either oversizing the oxygen production units or sourcing additional oxygen from other on-site processes where surplus oxygen is available. These adjustments ensure stable oxygen supply, preventing inefficiencies in the oxidation reactions that drive nitric acid production.

However, ammonia plants often support multiple production pathways, such as urea manufacturing. In these cases, the oxygen balance shifts positively, even resulting in an excess oxygen supply.

4.4 N_2O emission reduction

Nitrous oxide (N_2O) emissions from nitric acid plants are a significant environmental concern due to their impact on climate change. N_2O is a potent greenhouse gas with a global warming potential approximately 273 times that of carbon dioxide (CO_2), making its mitigation critical for reducing industrial contributions to climate change. In nitric acid production, N_2O is generated as a byproduct of the ammonia oxidation process in the Pt/Rh gauzes (see reaction 5 in Section 3). Without proper abatement technologies, large quantities of N_2O can be released into the atmosphere, aggravating global warming. A nitric acid plant without N_2O abatement system would emit around 6 kg N_2O/ton HNO_3(100%).

To address this issue, many countries and regulatory bodies have implemented strict emissions limits and penalties for exceeding permissible N_2O levels. In the European Union, for example, nitric acid producers must comply with the EU Emission Trading System, which imposes costs on industries emitting excessive greenhouse gases, including N_2O. Facilities that fail to meet established emissions thresholds are required to purchase carbon credits or invest in emission reduction technologies, increasing expenses. Additionally, local governments may enforce specific penalties or restrictions on plants that do not adopt effective abatement measures.

Beyond financial penalties, there is growing pressure from international climate agreements, such as the Paris Agreement, to encourage industries to reduce their greenhouse gas footprints. Many nitric acid producers therefore invest in advanced abatement catalysts and process optimization technologies to lower N_2O emissions, ensuring compliance with environmental regulations while improving sustainability.

In the nitric acid industry, discussions around N_2O emissions often center on abatement technologies, which serve as remediation solutions for reducing environmental impact. While these approaches are effective, the underlying challenge lies in the fact that N_2O emissions must not only be controlled but fundamentally mitigated at the source. The Total Recycle concept incorporates an innovative approach to N_2O mitigation, ensuring destruction of N_2O within the process to prevent accumulation. To achieve this, a secondary catalyst is strategically placed beneath the platinum (Pt) gauzes, facilitating the breakdown of N_2O before it can build up within the system. Unlike conventional nitric acid plants, which continuously discharge tail gas containing residual N_2O into the atmosphere, the total recycle concept eliminates the need for such emissions. With no persistent tail gas flow exiting the system, the environmental footprint of N_2O is reduced to near zero (only small purge), significantly lowering greenhouse gas contributions.

In the European context, CO_2 emissions are subject to a penalty of approximately €88 per ton (as per January 2026). Since N_2O has a global warming potential 273 times that of CO_2, emitting one ton of N_2O incurs a significantly higher cost, estimated at around €24,024.

Even conventional nitric acid plants equipped with the most advanced abatement reactors still emit approximately 0.120 kg of N_2O per ton of HNO_3 produced (considering extremely low values, 20 ppm (vol), of N_2O in the stack). When translated into financial terms, this corresponds to an estimated penalty of around €3 per ton of HNO_3 with current carbon emission penalties.

5 COST ANALYSIS

5.1 CAPEX

CAPEX refers to the upfront investment required for the construction of a new nitric acid plant or the expansion of an existing facility. These costs comprise essential components such as equipment procurement, material sourcing, and labor expenses associated with engineering, fabrication, and installation. CAPEX represents a significant financial commitment, as it lays the foundation for long-term operational efficiency and production capacity.

Investing in a nitric acid plant involves strategic financial planning to balance initial costs with long-term economic benefits.

Although advanced technologies and regulatory compliance often lead to higher CAPEX, the Total Recycle concept presents an exception. Unlike conventional nitric acid plants, this innovative approach significantly reduces CAPEX while simultaneously enhancing operational efficiency, minimizing emissions, and lowering ongoing OPEX over time. This cost-effective solution demonstrates that strategic process optimization can lead to both economic and environmental benefits without requiring extensive upfront investment.

Several cases have been analyzed to perform a CAPEX comparison. All the cases have been evaluated for Europe:

- Case 1:
    - Total Recycle concept (pressurized oxygen) compared to the conventional mono-pressure plant (325MTPD)
- Case 2:
    - Total Recycle concept (pressurized oxygen) compared to the conventional dual-pressure plant (1000MTPD)
- Case 3:
    - Total Recycle concept with oxygen compressor compared to the conventional mono-pressure plant (325MTPD)
- Case 4:
    - Total Recycle concept with dedicated ASU for O_2 supply compared to the mono-pressure plant (325MTPD)

CAPEX REDUCTION (%) TOTAL RECYCLE vs CASES	
	CAPEX Cost Reduction
Vs Case 1	-34%
Vs Case 2	-25%
Vs Case 3	-26%
Vs Case 4	-7%

Table 1: CAPEX comparison for several cases.

As previously noted, the CAPEX of a Total Recycle plant is significantly reduced due to the elimination of the compressor train and the downsizing of the oxidation/absorption column. Additionally, the absence of a NO_x abatement reactor further contributes to cost savings. These advantages result in equipment costs being reduced by nearly half compared to a conventional nitric acid plant. Additionally, the simplified plant layout leads to a significant reduction in piping complexity and civil engineering requirements.

Even the case where an ASU is fully dedicated to supplying oxygen to the nitric acid plant seems attractive and shows lower capital investment than the conventional mono-pressure plant.

5.2 OPEX

OPEX refers to the recurring costs associated with maintaining and running a nitric acid plant. These expenses comprise raw material procurement, energy consumption, equipment maintenance, and labor costs necessary to sustain the continuous production process. Efficient management of OPEX is critical in optimizing profitability and ensuring long-term operational sustainability.

OPEX is influenced by several key factors, including the plant's operational efficiency, production volume, and external elements such as energy prices and regional regulatory requirements. Variations in these parameters can significantly impact overall expenditure, making it essential to evaluate and compare different production approaches.

In this context, the OPEX of Stamicarbon's Total Recycle concept has been evaluated in comparison to Stamicarbon's mono-pressure nitric acid production. It is important to mention that standard mono-pressure process from Stamicarbon is more efficient than other technologies available in the market due to more effective use of heat within the process, meaning that the OPEX for standard Stamicarbon nitric acid production process is lower than other conventional technologies in the market (-5%).

This assessment, conducted within European context, provides insights into cost-effectiveness and potential savings. Some of the key operational parameters include:

- **Total ammonia (NH_3) consumption –** A key determinant of raw material costs, influencing overall process efficiency.
- **Cooling water consumption** – Impacts energy efficiency and operational sustainability.
- **High-pressure (HP) steam export** – Represents potential energy recovery and utilization benefits.
- **Electricity consumption** – A major operational expense, dependent on equipment efficiency and power sourcing.
- **Precious metal losses** – Associated with catalyst degradation and overall yield.
- **N_2O emission penalties** – Assuming plants operating with abatement reactor, where abatement reactors result in emissions of <40 ppm (vol).

Other operational expenditures, such as labor costs required for plant operation, are assumed to be comparable across all scenarios and thus excluded from this analysis.

This evaluation of operating costs provides insights into how Stamicarbon's Total Recycle concept can improve the energy efficiency of the process compared to existing industry practices.

OPERATING PARAMETERS			
	Total Recycle[1]	Stamicarbon's mono-pressure plant	Units
Ammonia consumption	281.5	284	kg/ton HNO_3 (100%)
Cooling water, dT = 10°	85	110	ton/ton HNO_3 (100%)
HP steam export, 45 bar, 450°C	-1200	-1000	kg/ton HNO_3 (100%)
Electricity[2]	22	85	kWh/ton HNO_3 (100%)
Precious metal losses	Similar between concepts		mg/ton HNO_3 (100%)
NO_x emissions	<0.004	0.050[3]	kg/ton HNO_3 (100%)
N_2O emissions	<0.006	0.120[3]	kg/ton HNO_3 (100%)
N_2O penalties	-	+3[4]	€/ton HNO_3 (100%)

Table 2: Comparison between main operating parameters of Total Recycle concept and Stamicarbon's mono-pressure plant.

When comparing the new Total Recycle concept to Stamicarbon's mono-pressure nitric acid production process, potential OPEX savings of up to 25% can be expected. The cost savings are driven by two main factors: HP steam export, which can exceed 1,200 kg of steam per ton of HNO_3 produced (a steam price of 50 €/ton has been used in this analysis), and reduced electricity consumption.

The advantages become even more compelling when the Total Recycle concept is compared with other standard nitric acid technologies currently available on the market. Stamicarbon's standard nitric acid designs can export higher steam rates (450 °C, 45 bar) primarily because the tail gas is heated to 480 °C, whereas other technologies typically reach only about 430 °C. This higher tail gas temperature allows the expander to extract more power, resulting in lower steam consumption in the steam turbine. If an electromotor is used in the compressor train, the reduced steam demand translates into a proportional decrease in electrical power consumption by the motor. When benchmarking the new Total Recycle concept against other mono-pressure technologies with lower steam export capabilities, projected savings can exceed 30%.

[1] *Total Recycle concept has been calculated based on the case that oxygen is received pressurized and there is no associated raw material cost.*
[2] *Compressors running on electromotor in both cases.*
[3] *Considering a tertiary abatement reactor with outlet concentrations of 10ppm (vol) of NO_x and 20 ppm (vol) of N_2O.*
[4] *Considering a nitric acid plant in Europe with most efficient tertiary abatement reactor emitting 20 ppm (vol) of N_2O.*

5.3 Financial analysis

Using Case 1 and Case 4 (Section 5.1) as the baseline scenario, the net present value (NPV) analysis demonstrates that the Total Recycle concept significantly outperforms conventional mono-pressure and dual-pressure processes in terms of cash flow and investment recovery.

Total Recycle process is projected to achieve positive cash flow by Year 3, whereas a conventional mono-pressure plant is expected to break even only by Year 5 (see Figure 6).

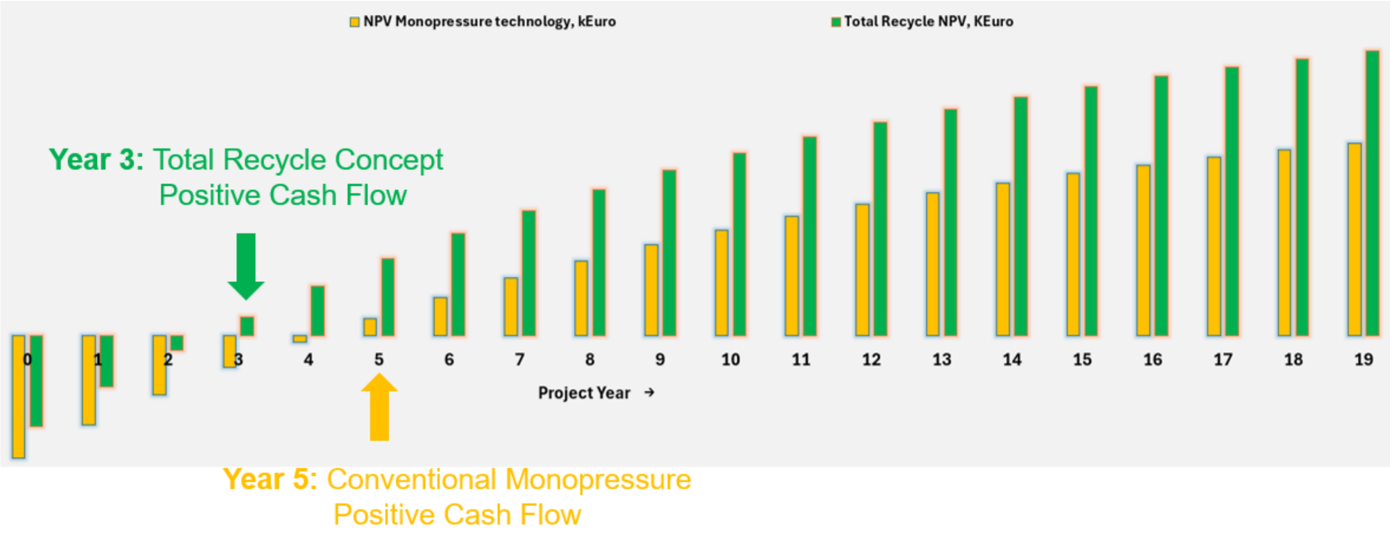

Figure 6: NPV analysis. Total Recycle and conventional mono-pressure concepts, 325 MTPD (100% HNO_3).

For higher capacities, Total Recycle process is projected to achieve positive cash flow by Year 2, whereas a conventional dual-pressure plant is expected to break even only by Year 3 (see Figure 7).

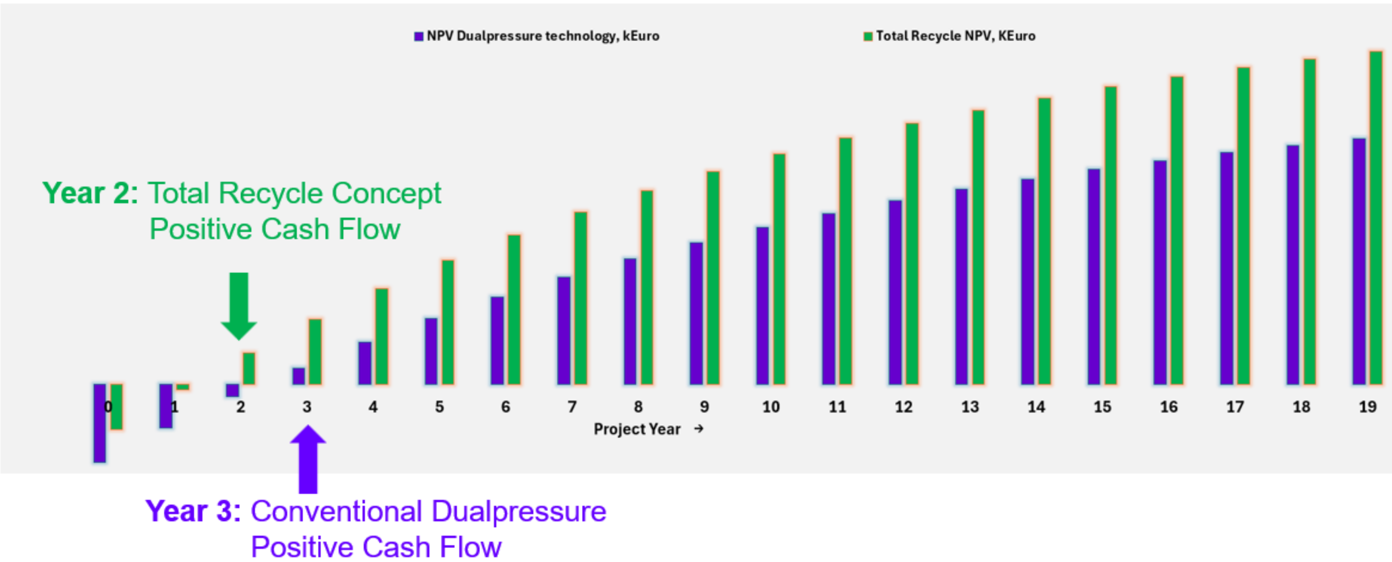

Figure 7: NPV analysis. Total Recycle and conventional mono-pressure concepts, 1000 MTPD (100% HNO_3).

Both analyses indicate a shorter payback period and stronger financial viability for the Total Recycle approach.

6 ALTERNATIVE APPLICATIONS OF OXYGEN

Other concepts can also be of interest when oxygen availability is limited or when the client's desire is to stick with more conventional ways of producing nitric acid. Here, two different types of alternatives are introduced.

6.1 Partial recycle concept

The partial recycle concept presents a particularly attractive approach when designing a mono-pressure nitric acid plant. In this setup, only a portion of the atmospheric air supply is replaced with synthetic air, which is generated by mixing oxygen with the necessary amount of tail gas—primarily nitrogen—maintaining a composition similar to atmospheric air.

To implement this concept, a fraction of the tail gas is recycled to the front section of the plant, while the remainder follows the conventional pathway, eventually being released into the atmosphere after undergoing purification in the N_2O/NO_x abatement reactor. The portion of recycled tail gas needs to be heated to the right temperature before being mixed with oxygen. Figure 8 provides a schematic representation of the partial recycle concept.

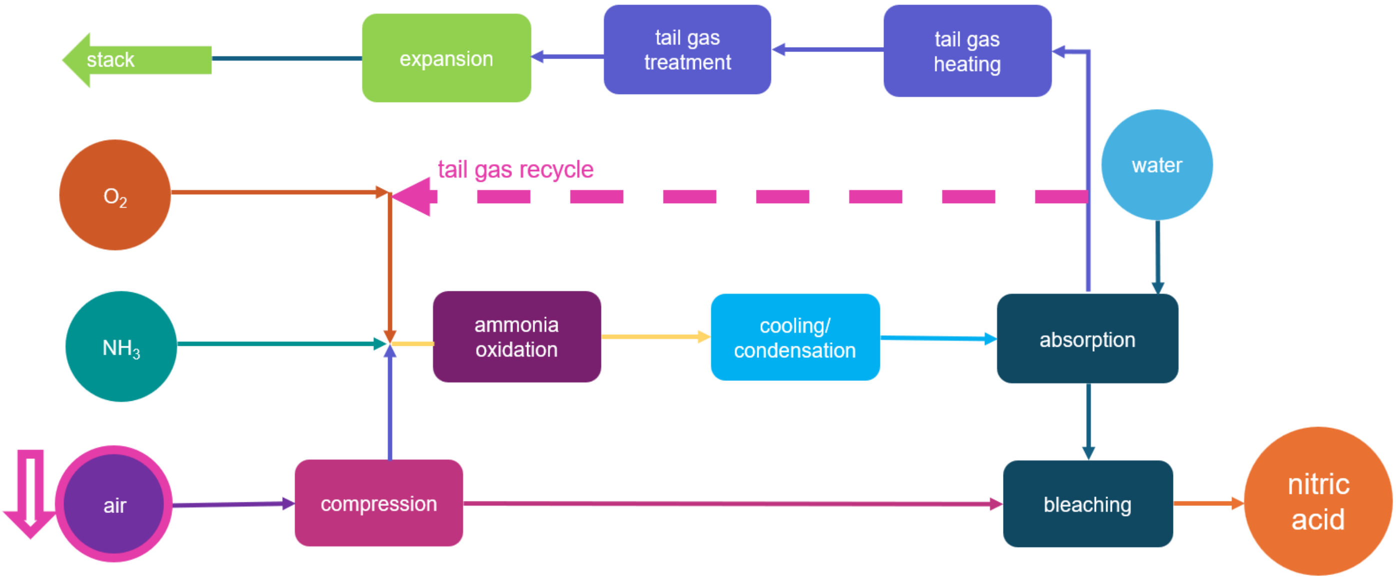

Figure 8: Basic block diagram of a mono-pressure nitric acid plant with tail gas recycling.

This concept offers several compelling advantages. First, recycling a portion of the tail gas helps reduce atmospheric emissions. While a tertiary abatement reactor is still necessary, reduced tail gas flow allows for a smaller reactor, leading to efficiency gains. Similar to the total recycle scenario discussed earlier, this approach also contributes to lowering N_2O penalties.

Second, generating synthetic air optimizes equipment sizing. The air compressor and tail gas expander can be scaled down, reducing costs across the compressor train. If the O_2 is supplied at high pressure, no additional O_2 compressor is needed. However, a booster compressor will be required to counteract the pressure drop associated with tail gas recycling in a mono-pressure plant.

Additionally, lowering the air flow through the air compressor—alongside the fact that not all tail gas must be heated to 480°C as in conventional setups—increases steam export.

This concept is particularly valuable for revamping nitric acid plants where O_2 is already available at battery limits. In such cases, the air compressor often poses capacity limitations, necessitating either an upgrade or the installation of an auxiliary air compressor. However, by utilizing synthetic air, the existing air compressor can continue operating at its current capacity.

Conversely, this approach is less beneficial for dual-pressure nitric acid plants. In these systems, tail gas recycling can occur without a booster compressor, thanks to the inherently higher tail gas pressure. However, redirecting tail gas to the front of the plant results in decompression and power loss that is not recovered, leading to lower steam export rates. Despite these drawbacks, advantages such as reduced emissions and smaller equipment size, particularly of the air compressor and tail gas expander, remain.

6.2 Oxygen injection through the bleacher

A simple yet effective method of utilizing available O_2 is injecting it directly into the bleaching column. This allows oxygen to fully or partially replace the secondary air typically used as a stripping agent.

As a result, the top gas outlet from the bleaching column becomes oxygen-rich, which is then redirected back into the process, where higher O_2 concentration enhances the oxidation of NO to NO_2 (see reaction 2 in Section 3). This improvement leads to higher oxidation efficiency in the cooler/condensers and the oxidation/absorption column, enabling a reduction in equipment size.

Like in the previous case, substituting secondary air with pure O_2 significantly reduces air compressor load, allowing for a smaller compressor. Additionally, if O_2 is received at high pressure, it eliminates the need for an O_2 compressor and increases steam export rates.

This approach enriches tail gas in oxygen. While conventional tail gas typically contains ~2 % by volume O_2, this concept increases oxygen concentration to up to 15% by volume. Tests on the abatement reactor have demonstrated that higher O_2 content does not affect the equilibrium between NO and NO_2.

Furthermore, this method provides a valuable strategy for plant revamping. By replacing secondary air with pure O_2, air compressor can be repurposed to supply more primary air to the burner, enabling an increase in plant capacity without significant investment.

7 CONCLUSIONS

Total Recycle concept for nitric acid production, which uses only ammonia (NH_3) and oxygen (O_2) while recycling nitrogen (N_2), offers significant advantages. It reduces plant complexity by eliminating the need for continuous air compression and decompression, leading to lower capital and operational costs.

Additionally, this method minimizes emissions of hazardous compounds such as nitrous oxide (N_2O) and nitrogen oxides (NO_x), contributing to a more sustainable production process. Total Recycle concept significantly reduces greenhouse gas emissions, particularly N_2O, which has high global warming potential. By incorporating a secondary catalyst to destroy N_2O within the process and avoiding accumulation, this method nearly eliminates N_2O emissions, making it a highly effective solution for mitigating environmental impact.

The CAPEX for nitric acid plants is a major financial consideration; Total Recycle concept significantly reduces this cost while improving efficiency and sustainability. Comparative analysis across several European cases shows that total recycle configurations can cut CAPEX by up to 34% compared to conventional plants, primarily due to simplified layouts and the elimination of costly components like compressor train and abatement reactor. Furthermore, this concept results in potential operational savings of up to 30% due to increased HP steam exports and reduced operational costs.

Other solutions that make use of pure oxygen have also been developed at Stamicarbon. On the one hand, there is the partial recycle concept, which involves recycling a portion of the tail gas to create synthetic air and acts as a good alternative when oxygen supply is limited. This approach reduces atmospheric emissions and optimizes equipment sizing, leading to cost savings and enhanced efficiency. It is particularly advantageous for revamping existing plants where O_2 is available, allowing for capacity increases without significant investment. On the other hand, injecting pure O_2 directly into the bleaching column increases process efficiency by enriching the gas stream with oxygen, improving NO oxidation, reducing compressor loads, and enabling smaller and/or more efficient equipment. This approach also supports plant revamping by freeing compressor capacity and allowing increased production without major investment.

These new concepts align with global efforts to transition towards more sustainable industrial practices. By increasing process efficiency and minimizing environmental risks, these methods support long-term viability of the chemical industry.

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